On the Dissociation Equilibrium of H_2 in Very Cool, Helium-Rich White Dwarf Atmospheres

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ABSTRACT

We investigate the dissociation equilibrium of H_2 in very cool, helium-rich white dwarf atmospheres. We present the solution of the non-ideal chemical equilibrium for the dissociation of molecular hydrogen in a medium of dense helium. We find that at the photosphere of cool white dwarfs of $T_{\text{eff}} = 4000\,\text{K}$, the non-ideality results in an increase of the mole fraction of molecular hydrogen by up to a factor of ~ 10, compared to the equilibrium value for the ideal gas. This increases the $H_2 - \text{He}$ CIA opacity by an order of magnitude and will affect the determination of the abundance of hydrogen in very cool, helium-rich white dwarfs.

Subject headings: dense matter – stars – atmospheres – stars: white dwarfs

1. Introduction

Several very cool white dwarfs with suspected $T_{\text{eff}} \lesssim 4500\,\text{K}$ have been discovered recently (Farihi 2005; Kilic et al. 2005; Gates et al. 2004; Oppenheimer et al. 2001; Harris et al. 2001; Hodgkin et al. 2000; Ibata et al. 2000; Harris et al. 1999). Most of them are thought to posses helium-rich atmospheres with an very high He/H $\gtrsim 10^3$ ratio (Bergeron et al. 2005; Kilic et al. 2005; Gates et al. 2004; Bergeron & Leggett 2002; Bergeron 2001; Oppenheimer et al. 2001; Hodgkin et al. 2000). In most cases, however, current atmosphere models fail to reproduce the observed spectra and photometry of these peculiar stars. The reason, and there may be more than one, for this shortcoming of the models is presently unknown. However, current models predict extreme physical atmospheric conditions for such stars, reaching densities of up to $2-3\,\text{g/cm}^3$. Under these conditions, the mostly ideal gas constitutive physics used in published atmosphere models is demonstrably inadequate. A careful look at the dense matter effects on the equation of state, chemistry, opacities, and radiative transfer is necessary to compute physically realistic models of these stars. Several of these ef-

fects have been studied previously, such as refractive radiative transfer (Kowalski & Saumon 2004), the effects of fluid correlations on He$^-$ free-free and He Rayleigh scattering (Kowalski et al. 2005; Iglesias et al. 2002), and the ionization of warm, dense helium (Kowalski et al. 2005; Bergeron et al. 1995). In this contribution we present an additional correction that arises in the dense fluid: The solution for the dissociation of molecular hydrogen in dense fluid helium, in the limit He/H $>> 1$. The relative importance of these corrections varies considerably, even more so when they are combined. As several more dense matter effects remain unexplored, it is premature to ponder their implications for the analysis of the coolest white dwarfs known and whether they will result in models that reproduce the data. Nonetheless, incorporating adequate constitutive physics in atmosphere models is a necessary step to reach a proper understanding of these peculiar stars.

We introduce non-ideal effects into the equilibrium dissociation of molecular hydrogen through a modification of the chemical potentials of H I and H_2 (section 2). We find that the strong interactions in the dense, helium-rich atmosphere results in a significant decrease in the dissociation frac-

tion of molecular hydrogen, with a corresponding change in the $H_2 - He$ Collision-Induced Absorption (CIA) opacity, which is linear function of n_{H_2}. In section 3, we illustrate the impact of the interactions on the $H_2/H\,I$ ratio on a sequence of white dwarf atmosphere models with $T_{eff} = 4000\,K$, a gravity of $\log g = 8$ (cgs), and a homogeneous composition of $He/H = 10^2, 10^4$, and 10^6, where He/H is the number abundance ratio.

2. The dissociation equilibrium of molecular hydrogen in a dense fluid

2.1. Theoretical approach

The condition for chemical equilibrium (at a given density and temperature) for the dissociation reaction:

$$H_2 \rightleftharpoons 2H\,I \tag{1}$$

is given by (Cox & Giuli 1968)

$$\mu_{H_2} - 2\mu_{H\,I} = 0, \tag{2}$$

where μ_i is a chemical potential of the species i expressed as

$$\mu_i = E_{0,i} + k_B T \ln \frac{n_i h^3}{Z_i (2\pi m_i k_B T)^{3/2}} + \mu_i^{non-id}. \tag{3}$$

In the above equation, k_B is the Boltzmann constant, h the Planck constant, T the temperature, $E_{0,i}$ the ground state energy, n_i the number density, Z_i the unperturbed internal partition function, and m_i is the mass. The first two terms on the r.h.s. of equation (3) represent the ideal contributions of translational and internal degrees of freedom and μ_i^{non-id} is the non-ideal contribution to the chemical potential arising from the interparticle interactions in the fluid. Setting $\mu_i^{non-id} = 0$ we recover the standard Saha equation for dissociation of molecular hydrogen:

$$\beta^{id} = \frac{n_{H_2}}{n_{H\,I}^2} = \frac{Z_{H_2}}{Z_{H\,I}^2} \left[\frac{m_{H_2} h^2}{2\pi m_{H\,I}^2 k_B T} \right]^{3/2} e^{D_0/k_B T} \tag{4}$$

where $D_0 = 2E_{0,H\,I} - E_{0,H_2} = 4.478\,eV$ is the dissociation energy of the isolated hydrogen molecule. Even for trace species, like $H\,I$ or H_2 in dense helium, the μ_i^{non-id} which arise from interactions with the atoms are not negligible and in principle should be comparable in magnitude to μ_{He}^{non-id}.

If we define the quantity ΔI as

$$\Delta I = \mu_{H_2}^{non-id} - 2\mu_{H\,I}^{non-id}, \tag{5}$$

the non-ideal equilibrium equation can be written in the following form

$$\beta = \frac{n_{H_2}}{n_{H\,I}^2} = \frac{Z_{H_2}}{Z_{H\,I}^2} \left[\frac{m_{H_2} h^2}{2\pi m_{H\,I}^2 k_B T} \right]^{3/2} e^{(D_0 - \Delta I)/k_B T}$$

$$= \beta^{id} e^{-\Delta I/k_B T}. \tag{6}$$

Comparing (4) with (6), we see that the non-ideal effects on the dissociation equilibrium can be *interpreted* as a change in the dissociation energy by a value of ΔI. For simplicity, we will follow this interpretation hereafter. We emphasize that this description of the non-ideal contribution to the chemical equilibrium (Eq. 6) is *identical* to the occupation probability formalism of Hummer & Mihalas (1988) if there is only one bound state in the partition function (e.g. low temperature $H\,I$) or if the $\mu_{i,j}^{non-id}$ is the same for all bound states j of the species i ($\mu_{i,j}^{non-id} = \partial f(V,T,n_{i,j})/\partial n_{i,j}$ remains constant in Eq. (2.17) of Hummer & Mihalas (1988)). In both cases, the occupation probability can be factored out of the partition function and written as $e^{-\Delta I/k_B T}$ (Eq. 6).

In the atmosphere of cool white dwarfs, hydrogen exist mostly as H_2 and $H\,I$, and the $H\,I/H_2$ ratio is governed by reaction (1) only. For a given temperature, density ρ, and the atmosphere composition $y = He/H$, the number densities of H_2 and $H\,I$ are:

$$n_{H\,I} = \frac{-1 + \sqrt{1 + 8\beta n_{tot}}}{4\beta}, \tag{7}$$

$$n_{H_2} = \beta n_{H\,I}^2, \tag{8}$$

where

$$n_{tot} = n_{H\,I} + 2n_{H_2} = \frac{\rho}{m_H + y m_{He}}. \tag{9}$$

refers to the hydrogen species only.

2.2. Computation of the H_2 dissociation equilibrium

The non-ideal contributions to the chemical potentials of $H\,I$ and H_2 were obtained through the numerical solution of the Ornstein-Zernike equation in the Percus-Yevick (PY) approximation
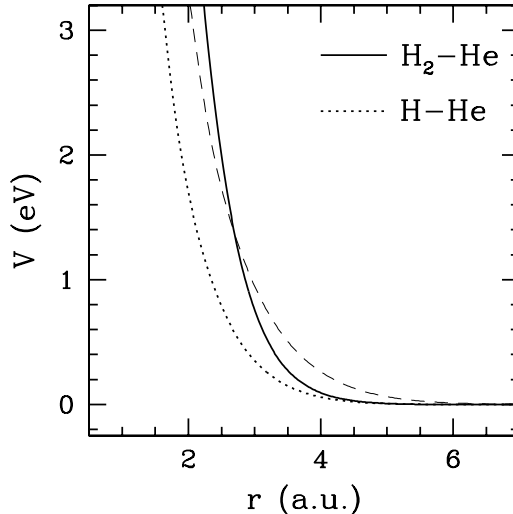
Fig. 1.— The H − He and H₂ − He pair interaction potentials. The dashed line represents the radius (horizontal axis) of a sphere whose volume equals the effective volume of two H atoms colliding with a kinetic energy of $\frac{3}{2}k_B T$ (see text).

(Martynov 1992). For the $H - He$ interaction we use the pair potential of Shalabi et al. (1998), and for the $H_2 - He$ interaction the pair potential given by Ree (1983) (Figure 1). Both potentials are from *ab initio* quantum mechanical calculations and are in good agreement with the independent calculations of Tang & Yang (1990) for $H - He$ and of Tao (1993) and Shafer & Gordon (1976) for $H_2 - He$. As we consider a helium-dominated mixture (He/H $\gtrsim 10^2$), the $H - H$, $H_2 - H$, and $H_2 - H_2$ interactions can be neglected.

High pressure experiments have shown that *ab initio* pair potentials are too repulsive to describe dense systems where N-body effects become important (Nellis et al. 1984; Ross et al. 1983). The softening of the pair potentials at high densities can only be quantified experimentally or, alternatively, estimated with N-body quantum mechanical calculations. Since neither are available for mixtures of trace hydrogen in helium, we resort to *ab initio* potentials. The net effect on the dissociation equilibrium depends on the *relative* softening of the potentials (Eq. 5) and is therefore less sensitive to N-body effects than the individual potentials. We also calculated the chemical potentials in the Hypernetted Chain approximation and found

them to agree within 5% with the PY values up to $2 \, \mathrm{g/cm^3}$. Since the PY approximation is better suited for short range potentials such as the ones we use here, we estimate that our PY calculations are reliable up to at least $2 \, \mathrm{g/cm^3}$.

For the internal partition functions Z_i, we use expressions for the electronic ground state of the unperturbed hydrogen molecule accounting for the vibrational/rotational excitations (Huber & Herzberg 1979), and set $Z_{H\,I} = 2$ for hydrogen atom. This approximation is justified as the electronic excitation energies of both species are large and for temperatures of a few thousands degrees the populations of the electronic excited levels are extremely small. However, there is significant thermal excitation of the rotational and vibrational levels of H_2 and the effect of the dense medium on Z_{H_2} must be considered. Since the molecule does not have spherical symmetry, it is possible that its rotation modes will be hindered by interactions with neighbors at very high density. Furthermore, the energies of the vibrational levels, which are spaced by a mere $0.54 \, \mathrm{eV}$, could also be significantly shifted by these interactions. Both of these effects are discussed by Saumon & Chabrier (1991) and can be neglected under the
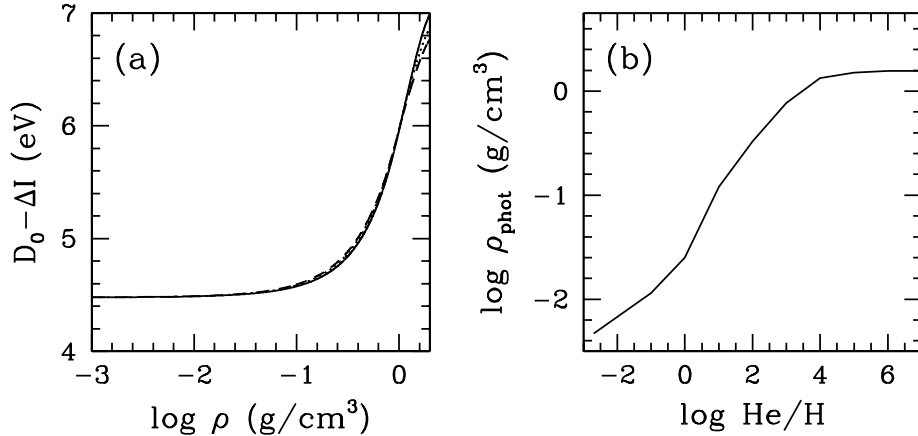
Fig. 2.— (a) Variation of the effective dissociation energy $D_0 - \Delta I$ as a function of the density of helium for temperatures of $3000\,\mathrm{K}$ (solid line), $4000\,\mathrm{K}$ (dotted line), and $5000\,\mathrm{K}$ (dashed line). (b) The density ρ at the photosphere of cool white dwarf atmosphere models of $T_{\mathrm{eff}} = 4000\,\mathrm{K}$, $\log g = 8$ (cgs), and various He/H compositions.

present conditions. The use of the unperturbed rotational and vibrational levels of H_2 is thus justified in the calculation of Z_{H_2}.

[hb]

More importantly, the excited rotational and vibrational levels of the H_2 molecule may be differentially affected by the interactions. This relates to the general problem of the cutoff of the sum over states in the internal partition function and is the subject of an extensive literature. This truncation of the partition function sum is often described by an occupation probability formalism (Hummer & Mihalas 1988) and in the case of interactions between neutral particles, is generally described in the context of the volume occupied by each bound state. In the case of a diatomic molecule, the volume occupied increases with the rotational quantum number (centrifugal stretching) and with the vibrational quantum number (larger amplitude of vibration). The first effect is very small and can be safely neglected. We estimate the vibrational stretching by considering the change in the equilibrium internuclear separation of the molecule with the vibrational quantum number. Because of the anharmonicity of the potential, higher vibrational levels correspond to larger equilibrium separations and a larger average molecular volume. Based on the potential curve of the H_2 molecule (Kolos &

Wolniewicz 1965) we find that for $T < 6000\,\mathrm{K}$ and densities of up to $2\,\mathrm{g/cm^3}$, the vibrational excitation is largely limited to the lowest five levels and the partition function is reduced by a few percent when the larger volume of the excited states is taken into account. This is a small effect which can be neglected in view of the other uncertainties in the model such as the N-body effects on the interaction potentials. Thus, the use of the internal partition function of the isolated H_2 molecule, with all states being affected identically by the interactions with He (Eq. 6) is a very good approximation.

3. Results and Discussion

3.1. The H_2 dissociation equilibrium in fluid helium

In general, the ΔI defined by (5) is a function of the density of helium and the temperature (Fig. 2a), but is independent of He/H ratio if H is a trace species (He/H $\gtrsim 10^2$). For the conditions in white dwarf atmospheres, the temperature dependence is weak. The change in the dissociation energy ΔI is negative, making H_2 more stable in dense helium. This may be qualitatively understood by comparing the effective volume occupied by one H_2 molecule to that of two H atoms in He.

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TABLE 1

THE CHANGE IN THE DISSOCIATION ENERGY ΔI (EV) FOR REPRESENTATIVE DENSITIES AND TEMPERATURES.

ρ (g/cm^3)	T(K) :	2000	4000	6000	8000
0.001		-0.001	-0.001	-0.001	-0.001
0.010		-0.007	-0.010	-0.011	-0.012
0.100		-0.083	-0.108	-0.120	-0.127
0.250		-0.242	-0.297	-0.323	-0.334
0.500		-0.579	-0.668	-0.697	-0.702
0.750		-1.006	-1.075	-1.088	-1.070
1.000		-1.471	-1.494	-1.469	-1.414
1.500		-2.011	-2.094	-1.963	-1.825
2.000		-2.189	-2.387	-2.192	-1.988

Lets assume that these effective volumes are the spaces around each of the particles where the energy of their interaction with He atoms is greater than the average thermal kinetic energy of the particles $\frac{3}{2}k_B T$. This radius is the classical distance of closest approach in a collision. On Figure 1, we plotted the radius of a sphere whose volume equals the effective volume of two hydrogen atoms, as a function of $k_B T$ (dashed curve). The corresponding radius for the hydrogen molecule is represented by the $H_2 - He$ potential (solid curve). The effective volume of H_2 is smaller than that of two H atoms for $k_B T \lesssim 1$ eV. Since the exclusion of a greater volume results in a decrease of the entropy of He, H_2 is more stable in dense helium than two H atoms. In dense hydrogen, we have the opposite situation where H_2 is less stable at high density (leading to pressure dissociation of H_2) because H_2–H_2 is more repulsive than the sum of the H–H and H–H_2 interactions (Saumon & Chabrier 1991).

Numerical values for ΔI obtained from our model are given in Table 1. Together with relations (6)–(9) this table allows for an easy implementation of the non-ideal abundances of atomic and molecular hydrogen into white dwarf atmosphere codes.

The non-ideal recombination of H becomes significant when $-\Delta I/k_B T \gtrsim 1$. For an atmosphere with $T_{\rm eff} = 4000$ K, this will occur at the photosphere if $\rho \gtrsim 0.3$ g/cm^3, a density easily achieved in He-rich models. As $D_0 - \Delta I$ increases with in-creasing helium density, a lower dissociation fraction will result. A strong deviation from the ideal-gas abundance of H_2 is expected.

3.2. The H_2 dissociation equilibrium in He-rich white dwarf atmospheres

We have applied the non-ideal correction to the H_2 dissociation equilibrium to very cool white dwarf atmospheres. To show the effect, we solved for the chemistry and opacity along fixed $T - \rho$ white dwarf atmosphere profiles of $T_{\rm eff} = 4000$ K, a gravity of $\log g = 8$ (cgs), and various He/H ratios. Figure 3 shows the atmospheric density profiles. These profiles were obtained with a code that solves for static, plane-parallel, and LTE white dwarf atmospheres in thermal and hydrostatic equilibrium, accounting for refraction (Kowalski & Saumon 2004). The resulting new abundances of H I and H_2 in our models are given on Figure 4 (left panels). As expected, the amount of molecular hydrogen increases significantly throughout the atmosphere for He/H $\gtrsim 10^3$, and H_2 can become the dominant hydrogen species at the photosphere.

The most important sources of opacity in helium-rich white dwarf atmospheres are He$^-$ free-free, Rayleigh scattering, and $H_2 - He$ CIA (Hansen 2004). Several physical and chemical effects that alter these opacity sources have already been discussed: the change in the free-free opacity and the Rayleigh scattering of helium, as caused by the strong correlations in the dense fluid (Igle-
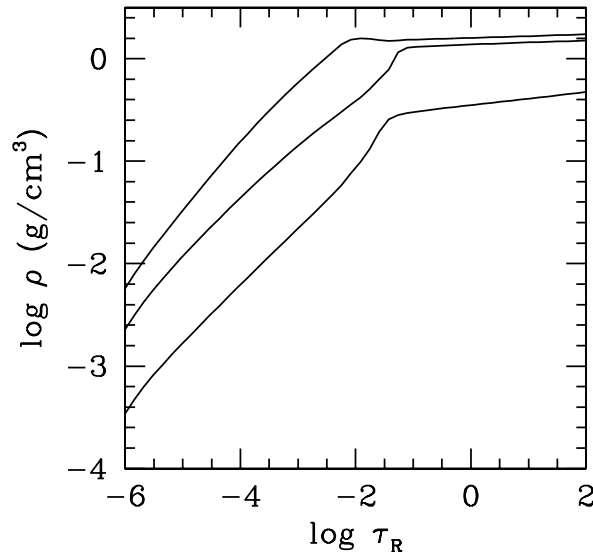
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Fig. 3.— The density profiles of white dwarf atmosphere models of $T_{\rm eff} = 4000\,{\rm K}$, $\log g = 8$ (cgs), and He/H composition of He/H $= 10^6, 10^4$ and 10^2 (from top to bottom, respectively).

sias et al. 2002), the change in the number density of free electrons (Kowalski et al. 2005; Bergeron et al. 1995), the presence of heavy elements (Bergeron 2001), and the formation of trace species like He_2^+ (Malo et al. 1999) and HeH^+ (Harris et al. 2004). The effect on non-ideal chemistry on the H_2 dissociation on the opacity is shown in the right hand panels of Figure 4. The increase in number density of molecular hydrogen results in an increase of the $H_2 - He$ CIA opacity. This follows from the linear dependence of $H_2 - He$ CIA opacity on n_{H_2}. On the other hand, the H^- bound-free and free-free opacities are reduced, due to the decrease in the abundance of atomic hydrogen. Based on the atmospheric structures used here, the effects of the non-ideal chemistry of H_2 in dense helium are maximal for He/H $\sim 10^3$. This arises from a competition between the need for a high He/H ratio to increase the non-ideal effects by increasing the density at the photosphere (Fig. 2b) and the need for a high enough hydrogen content in the atmosphere so that H_2 (or H) contributes to the total opacity (Fig. 4, right hand side).

The impact of the non-ideal dissociation equilibrium of H_2 on the synthetic spectrum of a He-rich white dwarf model is shown in Figure 5. For a white dwarf atmosphere model of $T_{\rm eff} = 4000$K, $\log g = 8$, and He/H $= 10^3$, the rise in abundance of H_2 increases significantly the opacity in the infrared, causing a redistribution of the flux toward shorter wavelengths. This effect on the spectrum of cool white dwarfs is largest for $T_{\rm eff} = 4000$K $- 4500$K, where H_2 is partially dissociated. At lower effective temperatures hydrogen exists mostly in molecular form and the effect of the non-ideal dissociation equilibrium on the spectrum vanishes at $T_{\rm eff} \sim 3000$K.

The determination of the He/H composition of very cool He-rich white dwarfs depends mostly on the relative $He - H_2$ CIA, and He^- free-free opacities (Fig. 4, right hand side), Since the non-ideal recombination increases the CIA opacity, this effect, taken by itself, will result in a higher value for the He/H ratio inferred from a given stellar spectrum. On the other hand, current calculations for the ionization fraction of dense helium and the low-frequency behavior of the He^- free-free opacity are uncertain and the He^- free-free opacity could be underestimated by as much as $\sim 2-4$ orders of magnitude (Kowalski et al. 2005). It is therefore too early to draw conclusions about
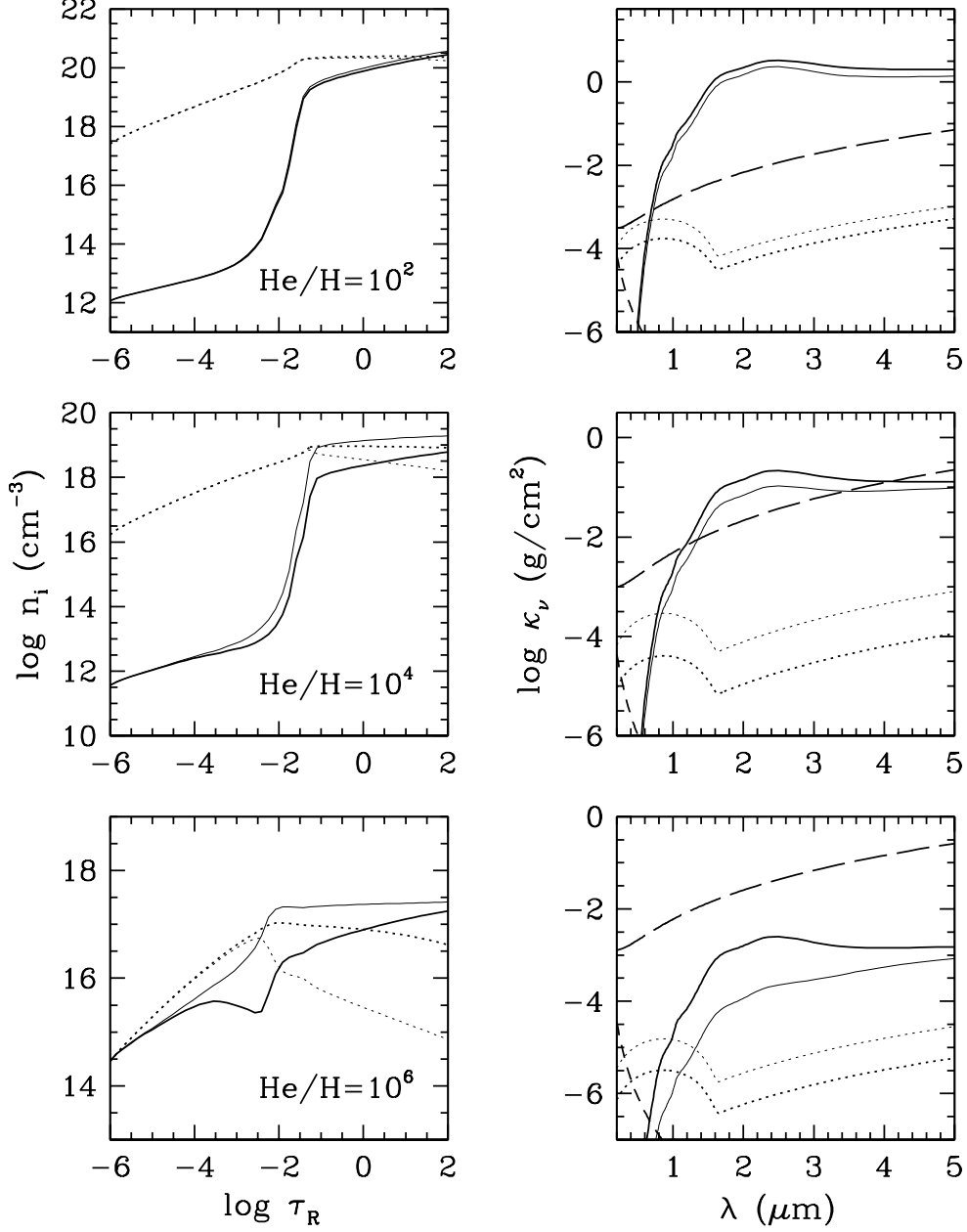
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Fig. 4.— Left panels: The number density of atomic (solid) and molecular (dotted) hydrogen with (thick lines) and without (thin lines) the non-ideal chemical equilibrium along the atmosphere profiles of Figure 3. Right panels: Corresponding contributions to the photospheric opacity: $H_2 - He$ CIA (solid), He^- free-free of Iglesias, Rogers, & Saumon (2002) (long dashed), H^- bound-free and free-free (dotted) and Rayleigh scattering (short dashed).
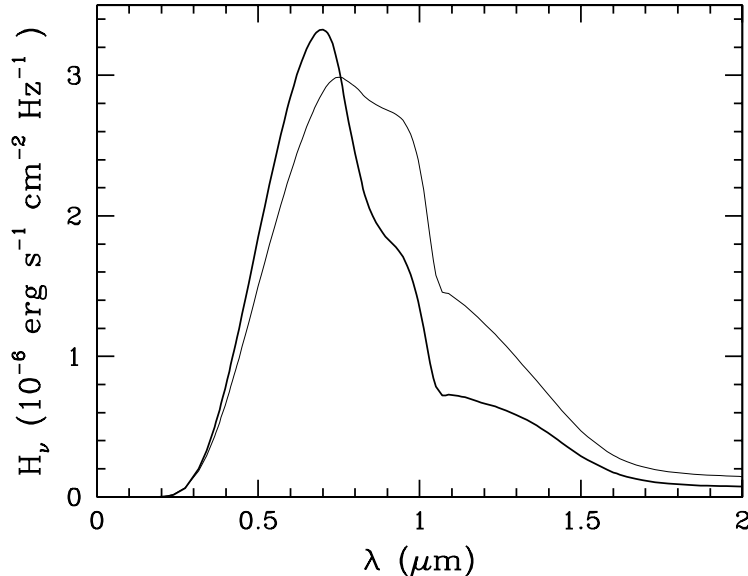
Fig. 5.— The synthetic spectrum for the white dwarf atmosphere models of $T_{\text{eff}} = 4000\,\text{K}$, $\log g = 8$ (cgs), and He/H $= 10^3$ with (thick line) and without (thin line) the non-ideal dissociation equilibrium of H_2.

the atmospheric composition of the coolest white dwarfs. However, we emphasize that, as the chemical equilibrium (6) is not affected by the number of free electrons in the atmosphere, our solution for the non-ideal abundance of H_2 will not be affected by weak ionization of He, and the results are limited only by the validity of the $H_2 - \text{He}$ and $H - \text{He}$ interaction potentials.

The non-ideal dissociation equilibrium in pure hydrogen atmospheres is discussed in Saumon & Jacobson (1999). As hydrogen is much more opaque than helium, the density at the photospheres of these stars is much smaller than for helium-rich atmosphere stars of the same effective temperature. The non-ideal effects are therefore weaker and become important only in stars of lower effective temperatures and/or higher gravity, where high densities are achieved. Saumon & Jacobson (1999) show that the non-ideality matters in pure-hydrogen atmospheres with $T_{\text{eff}} \lesssim 2500\text{K}$. White dwarfs with hydrogen-rich atmospheres of such low effective temperatures have not yet been identified.

4. Conclusions

Recent discoveries of a number of cool white dwarfs with peculiar spectral energy distribution represent a challenge in the modeling of very cool white dwarf atmospheres, as the spectra of these stars cannot be fitted with existing models. We believe that the main reason of this shortcoming of the models is the poorly explored, extreme physical regime found inside these atmospheres. We presented a correction to the abundance of H_2 that arises from the strong interaction of hydrogen molecules and atoms in a dense, fluid helium medium. We have found that in the dense, helium-rich, cool white dwarf atmospheres the formation of H_2 is more favorable than in the ideal gas description. For white dwarfs of $T_{\text{eff}} = 4000\,\text{K}$ and He/H $\gtrsim 10^3$ the abundance of molecular hydrogen increases by an order of magnitude, with a corresponding increase in the $H_2 - \text{He}$ CIA opacity by the same factor. This improvement is a new, significant effect that must be included in realistic modeling of very cool white dwarf atmospheres.

We have shown that the non-ideal effects affect strongly the abundances of even trace species in the atmosphere. This strongly suggest the ne-

cessity of revising the abundances of other trace species with significant opacity for similar effects. We expect that the study of their abundances and absorption processes in fluid helium will significantly improve our understanding of the atmospheric physics, composition, and evolution of the oldest and coolest white dwarfs.

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